APPLICATION

FOR

UNITED STATES LETTERS PATENT

TITLE: NON-SYMMETRIC CAPACITOR WITH ALUMINUM
CATHODE CURRENT COLLECTOR

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NON-SYMMETRIC CAPACITOR WITH
ALUMINUM CATHODE CURRENT COLLECTOR

5   Cross-Reference to Related Applications

This application is a continuation-in-part application of and claims priority to U.S.

Application Serial No. 09/358,577, filed on July 21, 1999, which is a continuation-in-part

of copending U.S. Application Serial No. 09/110,223, filed on July 6, 1998, and which

also claims priority from copending PCT Application Serial No. PCT/US99/15207, filed

10   on July 6, 1999.

Background of the Invention

This invention relates to non-symmetric electrolytic/electrochemical capacitors.

A typical symmetric aluminum electrolytic capacitor (FIG. 1) includes an

15   aluminum anode foil, an aluminum cathode foil, and a conductive liquid electrolyte, such

as ethylene glycol. Ethylene glycol is a substantially non-aqueous electrolyte, i.e. it

contains less than 3% of water. The liquid electrolyte is retained by a porous paper

separator which acts as a spacer between the anode and cathode foils. The anode and

cathode foils are connected to external terminals via aluminum tabs.

20   The surfaces of the aluminum anode and cathode foils are coated with a layer of

an insulating aluminum oxide, which is formed by an electro-chemical oxidation process

called forming. For the forming process, a constant voltage is applied to the aluminum

foils. The formation voltage is higher than a typical rated working voltage of the

capacitor. The aluminum oxide thickness is proportional to the applied voltage. In one

25   example, an aluminum electrolytic capacitor may have rated working voltages up to 600

V and forming voltages in the range of 850 to 900 V.

The insulating aluminum oxide is in contact with the conductive electrolyte. The

aluminum anode and cathode foils, the corresponding aluminum oxides, and the

electrolyte with the separator form two capacitors connected in series (FIG. 1A). The

30   thickness of the insulating aluminum oxide layer determines the breakdown voltage of

the capacitor. By varying the aluminum oxide layer thickness, the specific capacitance (i.e., capacitance per surface area) of each capacitor is varied. Increasing the aluminum oxide layer thickness reduces the specific capacitance and increases the breakdown voltage of the capacitor. The specific capacitance may be increased by increasing the

5   active surface area of the aluminum foil. The active surface area of the aluminum foil is increased by etching.

Another class of capacitors are the electrochemical capacitors. Electrochemical capacitors fall into two categories: Faradaic and non-Faradaic (double-layer). Non-Faradaic capacitors rely solely on interfacial charge separation across a boundary

10   between an electrolyte and a conducting surface or an insulating surface such as some metal oxides like aluminum oxide and tantalum oxide. The Faradaic capacitors are often referred to as pseudo-capacitors. Pseudo-capacitors have enhanced charge storage derived from charge transfer through a chemical reaction that takes place across the interface between an electrolyte and a conducting surface. The charge transfer can occur,

15   for example by: (1) surface charge attachment to a metal hydride like ruthenium hydride, (2) volume charge diffusion into a metal like silver coated palladium, or (3) an oxidation/reduction reaction at the surface of an oxide like ruthenium oxide. Non-symmetric electrolytic/electrochemical capacitors use a conventional electrolytic capacitor at the anode and an electrochemical capacitor at the cathode. Evans US

20   5,737,181 describes a non-symmetric capacitor that has a pseudo-capacitor ruthenium oxide ceramic cathode, a tantalum anode and an aqueous electrolyte. Non-symmetric capacitors with modified metal cathode surfaces are disclosed in Libby US 4,780,797 and Rogers US 4,523,255, which describe very aggressive aqueous electrolytes (e.g., sulfuric acid) that have high conductivity and are compatible with tantalum and tantalum oxide

25   anodes.

Summary of the Invention

In general, the invention features a capacitor of the type having a cathode and an anode and an electrolyte disposed between the cathode and the anode, the capacitor

30   comprising an electrochemical cathode comprising an aluminum current collector coated

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with a finely divided material, an electrolytic anode comprising aluminum coated with aluminum oxide, an electrolyte in contact with the finely divided material on the cathode and the aluminum oxide on the anode.

In preferred implementations, one or more of the following features may be incorporated. The electrolyte may be substantially non-aqueous. The electrochemical cathode may function by forming a double layer of charge at the interface between the finely divided material and the substantially non-aqueous electrolyte. The finely divided material may comprise carbon particles. The carbon particles may comprise at least one of carbon powder, carbon fibers, and graphite. The electrochemical cathode may function by the presence of an oxidation reduction reaction within the finely divided material. The electrochemical cathode may comprise a metal oxide coating. The metal oxide coating may be ruthenium oxide. The metal oxide may be hydrous amorphous ruthenium oxide powder adhered to the aluminum current collector. The cathode may further comprise an adhesion layer between the finely divided material and the aluminum. The adhesion layer may comprise a carbon rubber coating. The adhesion layer may be from 0.5 to 2.0 mil thick. The electrochemical capacitor may comprise a metal oxide adhered to the aluminum with the adhesion layer. The metal oxide may be hydrous amorphous ruthenium oxide powder. The substantially non-aqueous electrolyte may comprise an ethylene glycol solvent. The anode may have a larger surface area than the cathode.

Using an aluminum current collector provides a nonsymmetric electrolytic/electrochemical capacitor that performs well and that can be manufactured at lower cost.

Other features and advantages of the invention will be apparent from the following description of preferred embodiments, and from the claims.

Brief Description of the Drawings

FIG. 1 is a cross-sectional view of a prior art symmetric aluminum electrolytic capacitor.

FIG. 1A is an equivalent circuit diagram of a prior art symmetric electrolytic capacitor.

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FIG. 2 is a cross-sectional view of a non-symmetric electrolytic/electrochemical capacitor embodiment of the invention.

FIG. 2A is an exploded perspective view of another non-symmetric electrolyte/electrochemical capacitor embodiment of the invention.

FIG. 3 is a perspective view of an anode roll useful in some embodiments.

FIG. 4 is a cross-sectional view of a thin etched aluminum foil.

FIG. 5 is a perspective view of an expanded nickel mesh that may be used in the cathode.

FIG. 6 is a perspective view of the cathode collector coated with a finely-divided powder.

FIG. 7 is a diagrammatic view of a multi-cell non-symmetric electrolytic/electrochemical capacitor.

FIG. 8 is a flow chart of the process for fabricating a capacitor.

FIGs. 9A to 9D show impedance spectroscopy data for embodiments with a carbon coated nickel cathode, etched and formed aluminum anode and non-aqueous electrolyte.

FIGs. 10A to 10D show impedance spectroscopy data for embodiments with a ruthenium oxide coated titanium cathode, etched and formed aluminum anode and non-aqueous electrolyte.

FIGs. 11A to 11D show impedance spectroscopy data for embodiments with carbon coated nickel electrodes (anode and cathode) and with butyrolactone based electrolyte.

FIGs. 12A to 12D show impedance spectroscopy data for embodiments with carbon coated nickel electrodes (anode and cathode) and with ethylene glycol based electrolyte.

FIG. 13A is a diagrammatic view of a double anode structure for an AC start capacitor.

FIG. 13B is a plot of the applied AC voltage across the double anode structure of FIG. 13A.

FIG. 14A is a diagrammatic view of a double anode with a floating capacitor structure for an AC start capacitor.

FIG. 14B is a plot of the applied AC voltage across the double anode with the floating capacitor structure of FIG. 14A.

FIG. 15 shows the process for winding an anode with multiple current collector sheets.

5   FIG. 16 is an end view of another non-symmetric electrolytic/electrochemical capacitor embodiment of the invention, in which both the anode and cathode layers are wound in the same winding. A portion of the winding is shown enlarged to provide a diagrammatic view of the cathode, anode, and separator layers.

FIG. 17 is a diagrammatic cross sectional view of a tiny portion of the

10   embodiment of FIG. 16, showing the cathode, anode, and separator layers in cross section.

FIG. 18 is a diagrammatic view of a multi-cell non-symmetric electrolytic/electrochemical capacitor wherein the anode layers are parallel to the cathode layers.

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Description of the Preferred Embodiments

FIG. 2 shows a first embodiment of a multi-section non-symmetric capacitor 50. Although only three capacitor sections 51a to 51c are shown for purposes of illustration, a typical embodiment may have more sections (e.g., 5 to 50, or many more). Each

20   capacitor section 51a includes an anode 52, a cathode 54, an electrolyte 58 (liquid that impregnates the capacitor or partially fills the interior of container 55), and separator disks 56. In one example, the anodes 52, cathodes 54, and the separator disks 56 have annular shapes with central openings 63, 65, and 67, respectively. The anodes 52 are interleaved with the cathodes 54, and the individual capacitor sections are stacked so that

25   a sequence of cathode/anode/cathode/anode is formed. The separator disks 56 separate the cathodes 54 from the anodes 52 within a capacitor section, and from the anodes in the adjacent capacitor section. The stacked sections 51a, 51b, and 51c are supported by a plastic support member 49, which is fed through the central openings 63, 65 and 67. The section assembly is placed in a plastic container or other suitable container, such as an

30   aluminum case 55 which is closed on the top with a cover 59. The cover has a vent 61

and anode and cathode voltage terminals 60a, 62a. The vent is configured to open when the pressure inside the capacitor exceeds a certain value, e.g., 75 psi.

The anodes 52 may be formed by splitting and winding etched and formed aluminum foil 82. For example, starting with a wide roll (in one example the width may be in the range between 50 to 100 cm), the material may be split (in one or more splitting steps) into 3-23 mm wide sheets, which are then wound to form a plurality of narrow rolls 80 (FIG. 3). Conventional processes may be used to etch the aluminum foil and form the aluminum oxide layer 84 (shown diagrammatically in FIG. 4). The etching process produces micron size holes 86 in the foil. The holes increase the effective surface area of the anode. In one example, the aluminum foil is 6 mm wide, and has a thickness of 100 micrometers. The etched aluminum holes 86 with the aluminum oxide layer 84 may be approximately 40 micrometers deep on both surfaces.

Alternatively, the anode may be fabricated by winding a flattened small diameter etched aluminum wire into a roll. The aluminum oxide layer is subsequently formed.

The insulating aluminum oxide surface of the anode contacts the electrolyte 58, to form an anode capacitor consisting of conductive aluminum/insulating aluminum oxide/conductive electrolyte.

The cathode 54 may be formed by coating a metal current collector with a finely divided material. A finely divided material is a conducting material or any material which supports an electrochemical capacitance at an interface with an electrolyte and has a very high ratio of surface area to volume. In some instances, the surface of the current collector is coated with a layer of a non-insulating oxide. The finely divided material provides the interface with the electrolyte which functions as an electrochemical capacitor. In one example, the thickness of the cathode is in the range between about 75 to 100 micrometers.

A variety of materials may be used for the cathode current collector. They include materials that do not oxidize, such as noble metals, platinum or palladium, or materials that form a conducting or a semiconducting oxide, such as nickel and titanium. If nickel is used, e.g., a nickel mesh as shown in FIG. 5, care should be taken to avoid an electrolyte in which ammonia is used, as this may produce corrosion in the nickel.

A non-insulating oxide forming current collector is required because if a thin insulating oxide layer develops between the high gain cathode capacitor and the current collector, it will contribute to the formation of an additional capacitor. The additional capacitor will be formed between the conductive current collector/insulating

5   oxide/conductive carbon powder. This additional capacitor will be connected in series with the electrochemical capacitor. When two capacitors are connected in series the capacitor with the smallest capacitance (in this case the additional capacitor) dominates and the benefit of the increased energy density of the electrochemical capacitor with the large capacitance diminishes.

10   The finely divided material, which together with the electrolyte forms the electrochemical capacitor, may be carbon powder, carbon fibers, graphite, platinum powder, oxide powders, such as ruthenium oxide, or mixtures of these powder materials. The material must provide a capacitor-like voltage/current relationship for the cathode.

The electrolyte 58 is a conducting liquid using either gamma-butyrolactone or

15   ethylene glycol as the major solvent. The gamma-butyrolactone is a substantially non-aqueous solvent, using an aromatic dicarboxylic acid/organic base as the major ionogen for conductivity. A cosolvent, such as methoscypropiomitrile, is added in concentrations up to 15% to modify low temperature characteristics. Specific depolarizers, such as benzyl, are added to reduce gassing, and organic phosphates to improve the oxide

20   stability. The ethylene glycol system is also a substantially non-aqueous electrolyte, and uses aliphatic dicarboxylic acids/ammonia as ionogens. A water content of 1.5 to 2.5% improves the oxide formation capability during aging and low temperature characteristics. Specific depolarizers, such as p-nitrobenzoic acid are added to reduce gassing, and organic phosphates to improve the oxide stability.

25   These electrolyte mixtures have very attractive properties for the aluminum anode. These include ability to form an insulating oxide layer through aging on the cut anode surfaces, long shelf life, ability to withstand high surge voltages, both low and high temperature performance with a small temperature coefficient, strong gas absorption properties to provide long service life, and ability to work with low cost separators. The

30   electrolyte mixtures also work well with many of the possible cathodes (e.g., titanium

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with a ruthenium oxide or carbon powder coating), even though they are non-aqueous and have a near neutral ph.

A presently preferred cathode is titanium printed with hydrated amorphous ruthenium oxide as disclosed in U.S. Patents Nos. 5,600,535 and 5,621,609, granted to the United States of America on February 4, 1997 and April 15, 1997, respectively. Such a cathode will work with the above-described ethylene glycol electrolyte. The cathode may also be constructed by printing ruthenium oxide on another current collector material (e.g., aluminum). The titanium substrate is preferably a foil about 12.5 to 50 micrometers thick (preferably 25 micrometers), which may be in the form of individual sheets or a roll.

Printing is accomplished by first coating both sides of the titanium with a conductive adhesion layer, e.g., a Rexam (TM) carbon-rubber material produced by the COER-X process (material available from Rexam Graphics, South Hadley, Massachusetts). The adhesion layer should provide a highly conductive, but noncapacitive, surface onto which the ruthenium oxide may be deposited. The surface of the carbon-rubber coating has a roughness that allows the ruthenium oxide to remain adhered. The coating should be kept thin to minimize its resistance. A thickness of about 5 micrometers has been found to function well, but other thicknesses (e.g., 2.5 to 12.5 micrometers) can be used.

After the titanium foil has been coated with the carbon-rubber layer, hydrous amorphous ruthenium oxide powder is deposited onto the coated surfaces as a thin film (e.g., by screen printing) about 5 micrometers thick (other thicknesses, e.g., 2.5 to 12.5 micrometers may also be used). The hydrous amorphous ruthenium oxide has been mixed with a proton conducting binder, which serves to provide mobile protons to the hydrous amorphous ruthenium oxide and to bind the ruthenium oxide particles so as to maintain close interparticle contact to minimize internal resistance. Suitable proton conducting binders are organic polymers having a fluorinated backbone and terminal sulfonic acid carboxylic acid groups on a fluorinated chain pendant to said fluorinated backbone. A preferred proton conducting binder is a fluorinated material arising from copolymerization of tetrafluoroethylene and FSO2CF2CF2OC(CF3)FCF2OCF=CF2 (Dupont Nafion™ in an aqueous solution). More detail on depositing the hydrous

amorphous ruthenium oxide as a thin film can be found in Chen et al. U.S. Application No. 09/137,227, filed by T.B. Kim Technologies International, Inc., of Los Angeles, California. The hydrous amorphous ruthenium oxide thin film is preferably applied by screen printing, using a printing solvent to suspend the ruthenium oxide particles and

5   proton conducting binder. The ruthenium oxide is printed in a specific pattern matching the geometry of the stacked individual anode rolls, thereby reducing the amount of expensive ruthenium oxide that is used.

The cathode may also be constructed by adhering carbon powder to an aluminum current collector. Aluminum, which is already in use in the anode, has the advantage of

10   being fully compatible with the preferred nonaqueous electrolyte. The difficulty with using aluminum for the current collector of the cathode has been that aluminum tends to form an insulating passive oxide when exposed to air. Such an oxide layer is unacceptable, for it provides, in effect, a small further capacitor in series with the principal capacitance provided by the cathode and anode, thereby unacceptably lowering

15   the overall capacitance. By using aluminum foil on which carbon powder has been adhered without an intervening oxide layer, these problems may be overcome. One such carbon coated aluminum foil product is available from W.L. Gore, Microfiltration Technologies Group, Dallas, Texas.

A further alternative is to bond Rexam (TM) adhesion layer to an aluminum

20   cathode collector without an intervening oxide layer. Then, either ruthenium oxide or carbon powder may be applied.

Referring again to FIG. 2, the capacitor sections 51a to 51c are connected in parallel to each other. The aluminum anodes 52 are spirally wound disks of standard etched and formed aluminum, about 100 Tm thick, 50 mm in diameter, and 6.3 mm wide.

25   The material can be obtained from a variety of sources (e.g., Aerovox, Beckermel, Satma, or JCC). A plurality (e.g., 3 to 10) of layers of aluminum are wound together and electrically connected in parallel so as to reduce the overall resistance of the anode for the same overall capacitance.

Electrical connections to the anodes are made using metal tabs 53 (small pieces of

30   soft aluminum) mechanically attached between the brittle anodes and anode leads 60. The anode leads 60 are lightly etched and formed aluminum. Cathodes 54 also have

metal tabs 57, which are ultrasonically welded to a cathode lead 62. The cathode lead 62 is preferably soft aluminum. The anode and cathode leads 60 and 62 are connected to the voltage terminals 60a and 62a, respectively, located on the top cover 59.

5   The separator disks 56 may be constructed from standard duplex or plain kraft paper or similar materials like Manila or Hemp (e.g., 50 - 200 micrometers thick). Other separator materials which can be used with the butyrolactone electrolyte mixtures and the ethylene glycol electrolyte mixtures include Kraft, manila or hemp fibers, or composites made from other paper separators and polypropylene fibers.

The much higher capacitance of the cathode compared to the anode allows the
10   cathode to have a much smaller surface area, e.g., 0.2% to 2% of the area of the anode.

FIG. 7 shows an alternative multi-section capacitor 50, which includes cathodes 54, separators 56, collector plates 61, and cubic anodes 52, which are formed as stacks of etched and formed aluminum sheets 52a. The aluminum sheets 52a have a rectangular shape. The cubic anodes 52 can be built in a progressive cut-to-length line with two
15   degrees of freedom. The stacked, etched, and formed aluminum sheets 52a are spot welded using a laser dot matrix pattern or ultrasonic welding. The cathodes 54 are shown as sheets of material that are interleaved between separators 56 and anodes 52. The collector plates 61 are conductive material conductively adhered to the ends of the individual aluminum sheets 52a.

20   This construction further reduces the series resistance and provides an attachment point for the anode lead 60, which can be spot-welded to each of the individual anode collector plates 61. This construction puts all the individual anode sheets 52a in parallel and leads to a further reduction in the series resistance.

This multi-section capacitor 50 with anodes constructed from stacked aluminum
25   sheets may be assembled using automated assembly equipment fed from two spools of material. One spool provides the cathode material which may be titanium printed hydrous amorphous ruthenium oxide. The second spool provides the anode material which may be a spool of very narrow etched and formed aluminum.

Other geometric configurations for the anode are possible. The stacked sheets
30   may be oval or circular. Multiple layers of aluminum may be rolled simultaneously to form anode rolls (as shown in FIG. 15), with each layer electrically connected in parallel.

This has the same effect as connecting layers of a stack in parallel. Overall resistance of the anode is reduced for the same overall capacitance.

The butyrolactone and ethylene glycol electrolyte systems are compatible with various polymeric materials (e.g., nylon and polypropylene), thus adding to the low cost

5 packaging options that can be obtained through this approach. This total package has the advantages of providing a very economical capacitor, using a set of materials that have a long field history under electrochemical conditions within a broad temperature range, and providing the basis for a new capacitor with the same long service life under electrochemical conditions.

10 Referring to FIG. 8, one process of making the capacitors includes the following steps: First, the anodes and cathodes are fabricated, and the separator disks are cut. The anodes, separators, and cathodes are then interleaved to form a stack. Anode and cathode tabs are ultrasonically welded to the anode and cathode leads, respectively, and the stack assembly is placed into a container. The anode and cathode leads are then connected to

15 anode and cathode voltage terminals, respectively, located on the container cover. The stack assembly is vacuum impregnated with a substantially non-aqueous electrolyte. The container is closed with the cover, additional electrolyte may be added, and the capacitor is aged at a rated voltage (e.g., 50 V DC) and elevated temperature (e.g., 85 EC). Finally, the vent is sealed, and the capacitor performance is evaluated by bridge measurements

20 and DC leakage current measurements at rated voltage.

Another multi-section capacitor construction is shown in FIG. 2A. The aluminum anodes 52 are arranged in groups (e.g., eight are shown) in the same layer, rather than having only a single anode in each layer, as in FIG. 2. Leads from each anode are connected to anode lead 60, which leads to terminal 60a on the cover 59. The cathodes

25 are titanium with hydrous amorphous ruthenium oxide printed in circular areas aligned with the aluminum anodes; cathode leads 62 connect the cathode sheets to terminal 62a on the cover 59. The stack of aluminum anode layers and cathode layers fits within a rectangular-shaped housing 55. Insulating separator sheets (not shown) formed from the same materials as discussed above for separator disks 56 are positioned between the

30 anode and cathode layers. Although circular anodes and matching circular cathode areas are shown in the figure, it may be preferable to use other shapes to increase the density of

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the capacitor; e.g., oval shaped anodes and matching oval shaped cathode areas could be substituted.

The assembly is formed by stacking the various components, i.e., separator material (one to three sheets typically), one layer of titanium coated foil, separator material (one to three sheets typically), an array of 8 anodes (two columns and 4 rows) with the tab material leads adhered together to form one lead per layer, separator material (one to three sheets typically), one layer of titanium coated foil, etc. The assembly may contain a number of layers (e.g., 10 to 20). The geometry of the capacitor can be varied and there is no standard number of anodes in an array and there is no standard or preferred number of stack layers in a complete assembly.

The individual anode layers and cathode layers are connected in parallel by adhering the individual aluminum leads to an aluminum bar across the top of the assembly. The assembly resembles a block, which is approximately 9 cm by 11 cm by 24 cm. Polypropylene insulation (18 Tm) is wrapped around the rectangular assembly and held in place with electrical tape. The two aluminum bars (one for the cathode connections and one for the anode connections) contain holes, which are bolted to the terminals in the cover (one for the anode and one for the cathode). The cover assembly is fabricated from a punched sheet of 40 mil food grade aluminum stock, folded and welded with holes for aluminum ceramic terminals. The cover assembly also contains a small vent hole which is sealed with a rubber plug after impregnation. The cover assembly with the capacitor is purshed down inside of an aluminum can, which has also been fabricated from food grade aluminum sheets. The cover assembly is welded to the top of the aluminum case. The complete capacitor (vent plug open) is impregnated in electrolyte using a standard vacuum-pressure impregnation oven. The impregnated capacitor is then aged using a standard oven aging power supply. The capacitor after aging is cooled to room temperature and the vent plug is sealed into the capacitor.

Referring to FIGS. 16 and 17, another construction for the non-symmetric capacitor has anode layers 52, cathode layers 54, and separator layers 56 wound in the same roll. A single such roll could form the capacitor, or multiple rolls could be connected together internally. The enlargement of the end of the winding in FIG. 16 shows the various layers, as does the cross sectional view in FIG. 17, which shows an

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enlargement of a tiny area of a cross section through the winding of FIG. 16. The anode and cathode layers are constructed as taught for the other disclosed embodiments, with one important exception. The anode layers are tunnel etched, so that tiny etching holes extend substantially fully through each anode layer. The tunnel etched holes are coated

5   with aluminum oxide in a forming process. MacFarlane U.S. Patent No. 5,584,890 discloses a symmetric electrolytic capacitor in which both anode and cathode are oxide coated aluminum, and the tunnel etching is provided in one of the anode and cathode.

In this alternative embodiment, the tunnel etching provides a path for conductive ions to flow between the cathode layer and anode layers. Three anode layers 52 separated

10   by spacer layers 56 from a single cathode layer 54 are shown. But varying numbers of anode layers (preferably between 1 and 7 layers) could be interspersed between each cathode layer. And the cathode layer could be formed by providing a plurality of adjacent cathode layers.

The arrangement of FIGS. 16 and 17, in which cathode and anode layers are

15   wound together, is preferred over the arrangement of FIGS. 1 and 2A, in which anode windings are interspersed between cathode sheets, as the width of the winding becomes greater. It appears that it may be preferable to use the arrangement of FIGS. 16 and 17 when the width of the winding (e.g., about 6 mm in FIGS. 2 and 2A) is greater than about seven times the aggregate thickness of the anode layers (e.g., each anode layer is about

20   100 micrometers in FIGS. 2 and 2A). Otherwise, the arrangement of FIGS. 2 and 2A may be preferable.

FIG. 18 shows an alternative to the arrangement of FIGs. 16 and 17. The anode layers 52, spacer layers 54, and cathode layers 56 are stacked instead of wound. This permits a construction comparable to that of FIG. 7, but with the cathode layers built into

25   the stacks rather than oriented perpendicularly to the edges of the stacked anode layers. Tiny etching holes extend substantially fully through each anode layer 52 just as in the embodiment of FIGs. 16 and 17.

FIGs. 9A to 9D show the impedance spectroscopy of a non-symmetrical capacitor constructed with a cathode made of carbon coated nickel expanded mesh. FIGs. 10A to

30   10D show the impedance spectroscopy of a non-symmetrical capacitor constructed with a cathode made of ruthenium oxide coated titanium expanded mesh. In both cases, the

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anode is constructed from etched aluminum foil. The electrolyte is a butyrolactone system.

FIGs. 9A to 9D and 10A to 10D show plots of capacitance (9A, 10A), resistance(9B, 10B), impedance (9C, 10C), and phase angle (9D, 10D) versus frequency. These data demonstrate capacitor performance limited by the capacitance of the anode for frequencies that are less than 1 Hz for this specific design. The frequency limit may be changed by adjusting the design parameters of the capacitor, for example the carbon coating thickness and anode geometry.

The measurements in FIGs. 11A to 11D and 12A to 12D, show the performance of symmetrical capacitors having carbon coated nickel screen electrodes. In FIGs. 11A to 11D, the electrolyte is butyrolactone based and in FIGs. 12A to 12D, the electrolyte is ethylene glycol based. The curves demonstrate capacitive performance with both electrolyte systems.

One of the advantages of this non-symmetric capacitor is that it can be used for high voltage application without series construction. Conventional electrochemical capacitors are limited to low voltages (e.g., less than or equal to 4.5 V). Higher voltage capacitor ratings using electrochemical capacitor technology require series construction. Series construction of electrochemical capacitors leads to voltage sharing problems, high series resistance, and sealing problems (the individual series section must be isolated electrically).

Since the capacitor uses an aluminum electrolytic anode, voltages as high as 600 V DC can be applied to the anode. Most of the applied voltage is placed on the anode, by choosing the anode capacitance to be a small fraction of the cathode capacitance. The interleaving construction leads to anode sections, that are operated in parallel, not in series. This eliminates the voltage sharing problems, leads to a much lower series resistance, and eliminates the sealing problems.

The lower series resistance is important for high current pulsing applications and continuous ripple current applications. Low series resistance directly relates to an increase in the peak current, that can be pulsed through the capacitor. Low series resistance also relates to a lower power factor for continuous ripple current applications.

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Another advantage of the capacitor is increased energy density for the non-symmetric capacitor. The ability to operate with a very limited amount of cathode material leaves more room within the same size case for anode material. This leads to an increase in the energy stored in the capacitor by a factor of 2 to 3 over conventional electrolytic capacitors.

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A further advantage comes from possible construction differences. Conventional aluminum electrolytic capacitors require etched foils, which must have some mechanical strength and flexibility so they can be formed and wound on a high-speed automatic forming and winding machine. This limits the etching and therefore the specific capacitance of the anode foil and, in turn, the amount of stored energy.

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Another advantage of the capacitor is improved service life. In DC applications of conventional aluminum electrolytic capacitors, the leakage current and gassing of the aluminum foils (primarily at the cathode) can limit the life of the capacitor by forming internal gas pressure which vents and sets the life of the capacitor. With the capacitors disclosed, hydrogen gassing is typically reduced resulting in considerably extended life for the capacitor.

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Another advantage is improved time constant. Electrochemical capacitors are inherently slow devices (long time constant) because of the high contact resistance across the large porous active surface area of the electrodes. The thick porous oxide layer provides a long conducting path and many conducting interfaces, which lead to a very high resistance. The thickness of the cathode layer is designed so that the cathode capacitance provides the correct voltage across the anode. By substituting the thick porous layer with a finely divided powder coating the thickness of the cathode is reduced. This causes a reduction in the time constant. Shorter time constant can also be obtained by selecting the aspect ratio (surface area to volume ratio) of the specific carbon particles used in the coating on the nickel (or titanium) wire.

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Another important design variable with the interleaving construction is the width of the anode roll; the smaller the width the shorter the time constant. By using a narrow anode foil width, the time constant can be decreased to 5 milliseconds. This is still too slow for high ripple current computer grade applications, but it is suitable for high CV (capacitance and voltage) low ripple current computer grade applications. In addition to

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the reduced time constant, the capacitor has less than half the size of an electrolytic capacitor.

The interleaving construction also provides the basis for a new approach to start (AC) electrolytic capacitors. Start (AC) electrolytic capacitors operate for a relatively short period of time and have a power factor between 2.5 to 6.5% . Conventional electrochemical capacitors have a power factor higher than 10% at line frequency and therefore are not suitable for AC start capacitor applications.

Referring to FIG. 13A, a typical double layer structure AC start electrolytic capacitor 100 has two anodes 102 and 104 wound back to back and separated by a separator 106. The formed aluminum oxide on the anodes functions as a diode, i.e. acts as an insulator in the forward bias direction and as a resistor in the reverse bias direction (bias is the direction of the applied electric field compared to the direction of the formed polarization electric field). When an AC voltage V is applied across the structure 100, at any point of the voltage waveform, one anode is a capacitor and the other a resistor (FIG. 13B). Therefore, the structure 100 behaves like a capacitor with a high power factor due to the resistance of the second anode.

Referring to FIG. 14A, an AC start electrolytic capacitor, includes in addition to the two anodes 102 and 104 a floating cathode 108 interleaved between the opposite polarized anodes. Separators 106 separate the anodes from the cathode. The behavior of the double anode with the floating cathode structure is the same as the double anode structure (FIG. 14B) except that the floating cathode reduces the anode formation voltage and thus the aluminum oxide thickness on the anodes. The reduced aluminum oxide thickness results in reduction of the time constant, size and cost of the AC start capacitor.

Replacing the floating aluminum cathode with a floating electrochemical cathode provides the same reduction in the anode formation voltage and has the additional benefit of reduced weight and size.

What is claimed is: